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Pickling and Chemical Polishing Test for Corroded Carbonaceous Steel Restoration

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Abstract: Restoration of corroded carbonaceous steel sheets has been tested by pickling and chemical polishing techniques. For pickling, three acidic solutions at 10% volume; that are tartaric, phosphoric and oxalic acid have been used. For chemical polishing a solution of phosphoric acid 10% volume containing MnHPO_4 for different weight per litre was tested. Concerning pickling, the treatment duration time is longer for the organic acid solutions to pickle the same weight percentage of the coating oxide. Oxalic solution reveals to form a more protective complex that resists longer to corrosion; over 200 h while corrosion appears after 170 h for tartaric solution and 130 h on the treated samples. This stands from the structure of the complexes that present different adsorption mode of molecule of water. Introduction of MnHPO_4 in the phosphoric acid solution to ensure chemical polishing improves the restoration. The samples treated with a solution containing 10 g L^{-1} of MnHPO_4 does not present any mark of corrosion and neither any weight variation after more than 400 h exposure time. Manganese ions in the complex that forms on the surface of the sample play an important role by forming MnO which preferentially reacts with atmospheric oxygen to form other higher oxides degree preventing so the metallic phase from corrosion.

Key words: Corrosion, pickling, chemical polishing, surface treatment, restoration

INTRODUCTION

The industrial companies, manufacturers of articles in metallic materials are confronted in the tropical zone, with problems of storage for their raw material as well as finished semi products. This, because of atmospheric corrosion that, these materials undergo. In Côte d'Ivoire, a company of kitchen utensils out of carbonaceous steel which has cease its activity during nearly five years was taken again by investors. The stock of raw material as of the finished semi products had undergone the effects of atmospheric corrosion. With an aim of developing this stock, work for restoration was to be undertaken to know research of processes. These treatments should allow the removing of the oxide coatings in order to perfect the surface of these articles allowing their enamelling to make finished products of them.

Pickling is the treatment carried out on metal parts after machining to dissolve oils of lubrication, as well as the metal filling that covers the machined parts and evenly oxides on the surface in order to make them suited to any surface dressing. Pickling process consists into plunging the articles in an acidic low grade solution; around 5% for sulphuric acid for very short times (Lipper, 1945). Immediately after this treatment the articles have to support the surface treatment they have been prepared for.

Chemical polishing is a process also used to perfect the surface of metal parts (Hickling and Rostron, 1955; Beaujard, 1952) and other solid phase such as glasses (Zhernovaya and Onishchuk, 2003). For metallic parts, this treatment intervenes after scouring and confers on the metal parts a uniformity of surface by dissolution of the irregularities.

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Chemical polishing is carried out with baths much more complex which are subject of patent. Alumina and its alloys are industrially treated with the processes Brytal and Alsack (Aluminium Co of America; Brace, 1955). Copper and its alloys are also subject of chemical polishing (Pinner, 1953) and so are iron and its alloys for special application such as pre-treatment for hard nickering and the finishing of mechanic tools (Sachs and Odgers, 1956).

These two techniques of surface treatment were tested for the restoration of the corroded articles' surfaces. The objective is to dissolve the oxide coatings which cover the parts, in order to obtain perfect surface for enamelling. Therefore, we've given interest to divert pickling solutions and a very simple polishing one to determine their capacity to favour a good restoration of the corroded metal and the condition of such treatment.

MATERIALS AND METHODS

These experiments were carried out during the year 2005 in the authors' mentioned laboratories at the National Polytechnique Institute; (INP-HB). The investigations were undertaken on utensils in carbonaceous steel that have been improved by atmospheric corrosion during five years.

For data exploitation, we have defined physical values that are: surface of the samples and their weight variation. Parameters taken in account for these studies are the corrosion rate, the duration time of pickling or chemical polishing and duration time for corrosion to appear on the samples after treatment.

The articles were cut into samples of 10 to 30 cm² area. A virgin piece which surface and weight is known stands as reference. For this reference, a parameter ρ^o that is the ratio of the virgin piece weight to its surface is determined. The experimental value found was equal to 0.290 g cm⁻². With this value, the main weight M of the corroded sample is determined. M and the corrosion rate are given by the following relations:

$$M = \rho \times S \tag{1}$$

and

$$\tau_{\text{corr}} = \frac{M_i - M^o}{2 \times S} \times 10^4 \tag{2}$$

With M_i, the weight of the corroded pattern. Surface is doubled to take both of the sample in account. The 10⁴ factor is to give the corrosion rate for 1 M². The corrosion rate represents the weight of oxygen that is fixed per surface unit during corrosion process.

After treatment, the sample is weighted again and the variation expressed by the relation:

$$\Delta M = \frac{M_t - M_i}{M_i} \times 100 \tag{3}$$

With M_t the weight after treatment. The ΔM variation versus treatment duration permits the determination of time for a good restoration of the sample. After treatment, the sample is exposed to the atmosphere and regularly weighted. The variation is expressed by the relation:

$$\Delta M_{\text{ex}} = \frac{M_{\text{ex}} - M_t}{M_t} \times 100 \tag{4}$$

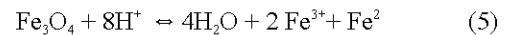
M_{ex}, the weight of the sample after exposition. ΔM_{ex} variation versus exposition duration will inform on resistance to corrosion.

Tartaric, oxalic and phosphoric 10% volume acid solution have been elaborated. The pickling treatments are undertaken at 60°C and the duration counted in minute while exposition time was taken in hour. These solutions should permit comparison between organic and mineral acid and two organic acids between them for the pickling process.

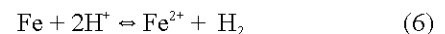
For chemical polishing, solutions constituted of MnHPO₄ for 10, 30 and 50 g L⁻¹ in a solution of phosphoric acid 10% volume have been tested in the same conditions on samples of corroded sheet with 150 g m⁻² corrosion rate.

RESULTS AND DISCUSSION

Pickling: Considering the representations of weight variation versus pickling duration; (Fig. 1 a-c), weight lost is sensitive to corrosion rate. This proves that oxide phases are dissolved by the acidic solution. Atmospheric oxidation of carbonaceous steel leads to an oxide essentially constituted by a melt of FeO and Fe₂O₃, giving Fe₃O₄. The dissolution reaction stands as:



During pickling, gas bubbles are produced. Protons reduction so occurs. The metallic phase is attacked to form hydrogen gas according to the following reaction:



For a good pickling, reaction 6 must be avoided. Therefore, acidic solutions usually used are very feeble; around 5%. But in the case of restoration that we need, solutions should have to be somewhat more acidic to favour reaction 5.

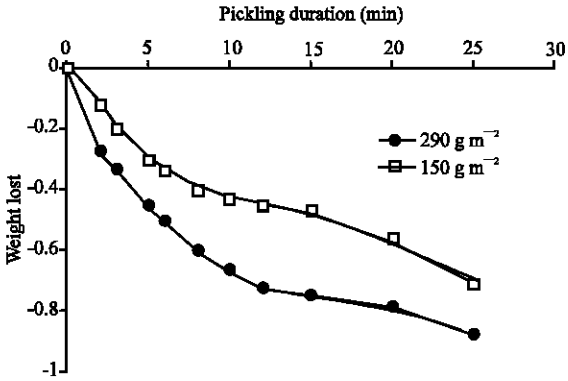


Fig. 1a: Weight lost variation for tartaric pickling bath

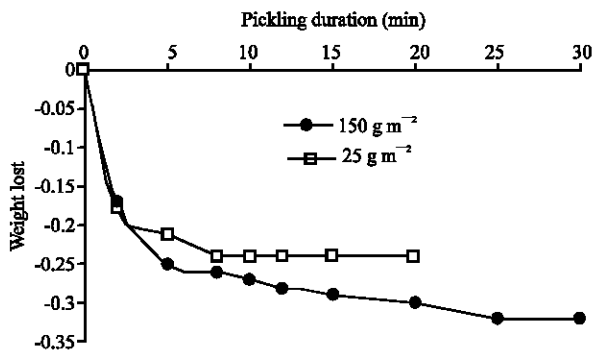


Fig. 1 b: Weight lost in oxalic pickling bath

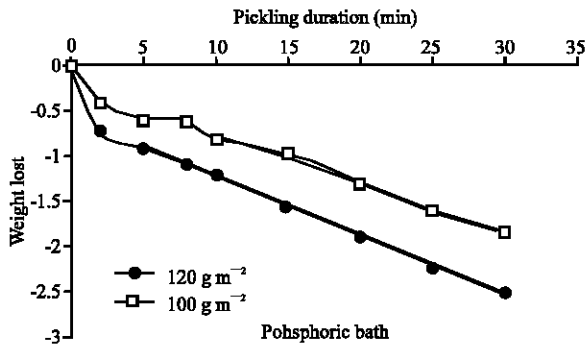


Fig. 1c: Weight lost for phosphoric pickling bath

According to representative graphs for tartaric and phosphoric acid solutions, (Fig. 1a and c) weight lost shape changes after a certain treatment duration time to adopt a negative slope that stays constant in each case. During this duration that is for 12 min in tartaric acid and around 5 min for phosphoric acid, reactions 5 and 6 stand. One can consider for both acid solutions that the weight constant decreasing prevailing after a certain time of pickling corresponds to reaction 6, when no more oxide has to be dissolved. So, knowing the slope should permit the determining of the weight lost part for each reaction

during the moment when both reactions stand. Nevertheless, during the first moments, the sample surface is mostly constituted of oxide phase so that reaction 6 should not prevail significantly.

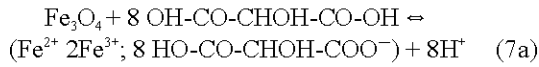
Calculation of the slopes gives -0.022 and $-0.055\% \text{ min}^{-1}$, respectively for tartaric and phosphoric acid for closed corrosion rate that are 120 and 150 g m^{-2} . Phosphoric solution seems so twice more aggressive than tartaric. The short pickling duration time noticed for phosphoric solution may be due to its higher aggressive character. The phosphoric acid first acidity pH value is of 2, while this appears for higher pH for the organic acid considered here. So reaction 6 favours pickling by diffusion of protons through the coating oxide phase to reach the metal. The hydrogen bubbles produced cause the detachment of the oxide phase accelerating so the pickling. This has been observed by the dispersion of oxide particles during the treatments with any solution. Reaction 6 is so responsible of pickling while reaction 5 assures dissolution of detached oxide particles.

Concerning oxalic acid Fig. 1b; weight lost does not increase with duration time after almost 10 min of pickling in contrary to the two first cases. Reaction 6 no longer takes place here. The weight lost is weaker in the organic acid baths for almost the same corrosion rate and pickling duration time is longer compared to phosphoric bath.

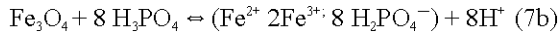
During oxidation, oxygen reacts with the metal, so the weight increasing of the corroded pattern corresponds to oxygen incorporated to form oxide phase. In example, for one of the patterns with 11 cm^2 area and 3.507 g weight for a corrosion rate of 145 g m^{-2} treated with tartaric acid, considering that the oxide phase is exclusively Fe_3O_4 , the incorporated oxygen should weight 0.317 g . The metal weight needed to form the considered oxide phase should be of 0.832 g . So the oxide phase that may be vanished by pickling is of 1.15 g . Nevertheless, after 12 min, when pickling is supposed to no longer take place, the weight lost is only of 0.48% that's to say 0.017 g of oxide have been vanished from the sample.

This noticing indicates that the reaction taking place maintains some species on the patterns. Those species could be resulting from reaction between the counter acidic ion and metallic ions Fe^{3+} and Fe^{2+} that are provided by reaction 5, to form a stable complex which remains at the surface of the sample. The weight variation between the metal after treatment and its weight if all the oxide phase was pickled should then correspond to the weight of the complex formed by the acid counter ions and metallic ions. So, after 12 min pickling duration, the complex formed weights 1.135 g . The reactions that lead to complexes forming in the three solutions should stand as follow:

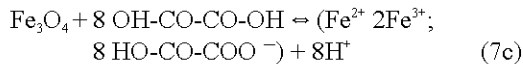
In tartaric solution;



In phosphoric solution;



And in oxalic solution;



For a mole of Fe_3O_4 concerned, in tartaric solution the complex formed should weight 1220 g and contains 168 g of iron so, proportionally the 1.135 g of complex formed on the sample should contain 0.156 g of iron that are maintained at the surface of the sample. As primarily indicated, the oxide phase formed on the pattern contains 0.832 g of metallic ion. Thereby, pickling should have dissolved 0.676 g into the solution, that to say 81% of the oxide phase has been vanished. The same approach with the pattern of 150 g m^{-2} corrosion rate treated with oxalic bath shows that 71.5% of the oxide phase is dissolved. For the patterns of 100 and 120 g m^{-2} corrosion rate treated by phosphoric acid, this approach indicates that almost 77% of the oxide phase is dissolved. These results expressed versus pickling duration time should reveal their efficiency. So the pickling efficiencies are respectively of 6.75, 7.15 and 15.4% min^{-1} for, tartaric, oxalic and phosphoric acid solutions. Phosphoric acid solution is from far more efficient than organic acid solution which efficiency are closed.

In the specific case of oxalic bath, formation of a complex perfectly stops weight lost even until 25 min pickling duration time. Reaction 6 does not occur while this takes place in the two other cases. That indicates that the complex formed with oxalate ion protects the metal from reaction 6. A passivation of the metal occurs. The phosphoric and tartaric complex doesn't prevent reaction 6. These complexes either permit diffusion of proton through that reach the metallic phase and form hydrogen bubbles that destroy them or they do not cover the all surface of the sample so that reaction 6 stands.

In conformation to pickling, organic acid baths reveal not to be the best for pickling; oxide phase dissolution being weaker than in the case the mineral acid. In another hand, reaction 6 that dissolved metallic phase and affects mechanic properties is prevented in the oxalic solution.

Polishing: In comparison to sample treated with phosphoric acid bath, those treated with the solutions

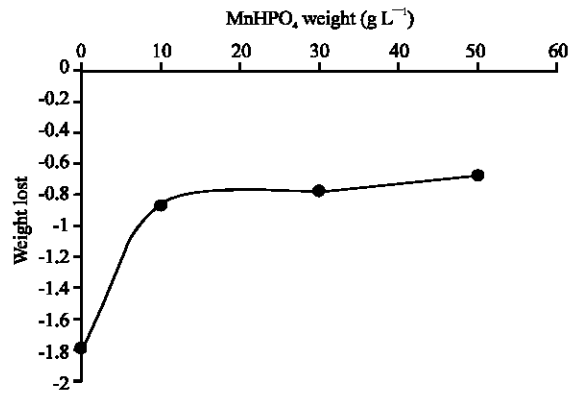


Fig. 2: Effect of MnHPO_4 on the weight lost in phosphoric acid (20 minutes duration time)

containing MnHPO_4 for 20 min duration present a lower weight lost for the same corrosion rate; Fig. 2. As already indicated, a complex forms and maintains species at the sample surface reducing then weight lost. Formation of this complex in presence of manganese prevents here from reaction 6 while this doesn't with the phosphoric pickling solution. The quantity of MnHPO_4 seems not to play a rule. In solution, the phosphate manganese is dissolved to free phosphate ions HPO_4^{2-} . According to reaction 5, the oxide phase is dissolved. Part of the metallic ions should form a complex with Mn^{2+} and HPO_4^{2-} that cover the surface of the sample.

Assuming HPO_4^{2-} ions to be more complexant with the iron ions, the complex formed for a mole of Fe_3O_4 can be formulated as: $(4\text{Mn}(\text{OH})_2; \text{Fe}^{2+}; 2\text{Fe}^{3+}; 4 \text{ HPO}_4^{2-})$. Considering the corrosion rate of the samples used, for 0.8% weight lost at equilibrium, the complex formed should weight 519 g for 1 m^2 . So the quantity of metallic ions in the complex is of 96 g and represents a fraction of 0.25. The fraction dissolved in solution is so much closed to the one determined for phosphoric solution; 0.75 and 0.77. Despite increasing fourfold of pickling duration time, the same proportion of oxide is vanished. The oxide vanishing is so due to the same mechanism that is diffusion of protons through the covering oxide phase to react according to reaction 6 and hydrogen bubbles cause its detachment. Manganese presence permit the forming of a complex that covers the surface of the pattern and prevents from proton diffusion. The weaker weight lost noticed is only due to the weight of the complex formed that contain manganese making it heavier.

This chemical polishing solution compiles of the good pickling of phosphoric solution on a short time and the forming of a passivating complex that protects the pickled surface from metal attack by the protons and also prevents it from corrosion.

RESISTANT TO CORROSION

Figure 2a-d inform on the resistance to corrosion of the samples after treatments. Figure 3a and b representing, respectively weight variation for samples treated with phosphoric and tartaric acid during exposure to atmosphere present the same shape. The weights significantly augment during the first 30 h for phosphoric treated samples and 70 first hours for tartaric treated ones. Then, it decreases to stabilises after around 130 h exposure time for phosphoric treated samples and around 170 h for the tartaric treated ones. These durations exactly coincide with corrosion appearing.

Weight increase noticed in both cases is consecutive to molecules of water adsorbed by the complexes that has been formed at the sample surfaces during pickling. Water adsorption leads to hydroxide by reacting with the metallic ions. This initiates the following cycle of reactions:

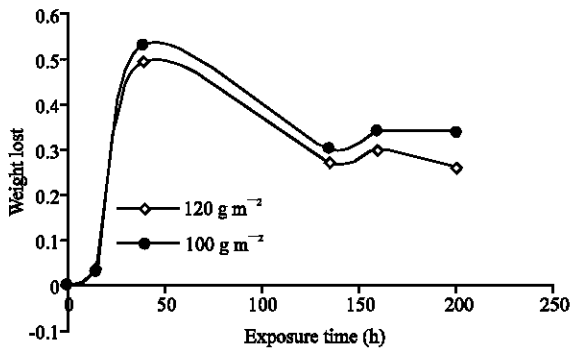
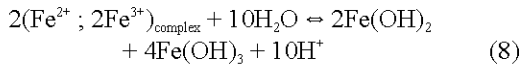


Fig. 3 a: Weight variation after pickling in phosphoric acid bat and exposure to atmosphere

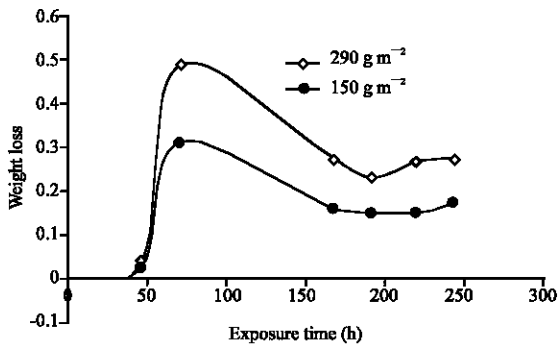
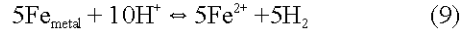
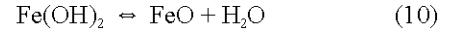


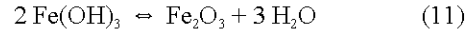
Fig. 3b: Weight variation for sample after pickling in tartaric bath and exposure to atmosphere



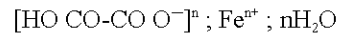
Reaction 8 causes the complex destruction and reaction 9 stands on the metal. Dehydration of the hydroxides occurs inducing weight decreasing with oxide phase appearing according to the following reactions:



and or:



For oxalic treated sample, hydration of the complex formed on the sample also occurs, but no dehydration seems to happen even after 200 h exposure time. The hydrated complex is so stable and prevent from oxide formation. The complex formed at the sample surface prevents it so from corrosion over more then 200 h after treatment. The structure of the complex can be as follows:



With Fe^{n+} being Fe^{2+} or Fe^{3+} .

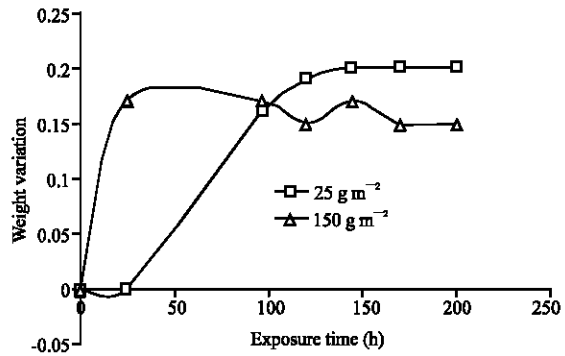


Fig. 3c: Weight variation after pickling in oxalic acid bath and exposure to atmosphere

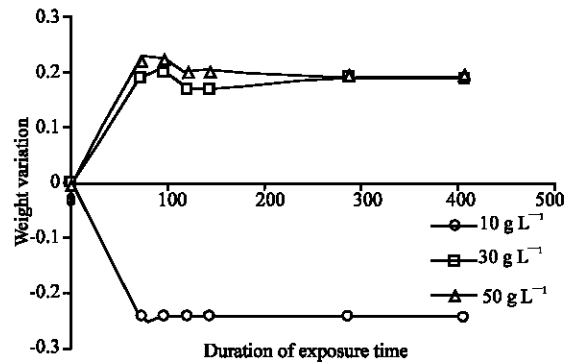


Fig. 3 d: Weight variation after polishing in MnHPO_4 in 10% phosphoric acid and exposure to atmosphere

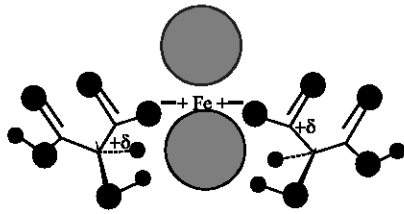


Fig. 4a: Scheme of complex formed with the tartaric acid and metallic ions

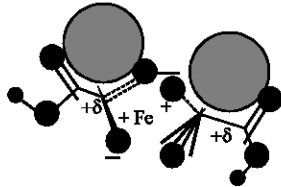


Fig. 4b: Scheme of complex formed with the oxalate ion and metallic ions

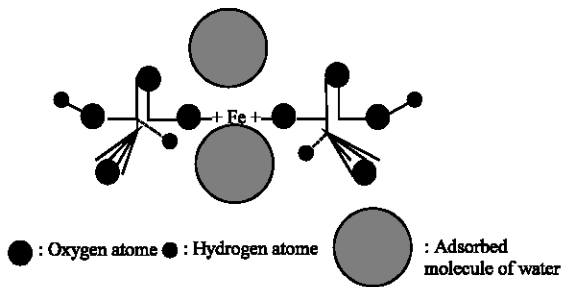


Fig. 4c: Scheme of complex formed with the phosphate ion and metallic ions

The carbon atoms, because of the neighbourhood of oxygen present a high electrophilic character and the oxalate ion geometry permit adsorption of a molecule of water on; Fig. 4b. The metallic ions positive charges are then stabilized by the negative oxygen ones, so that they do not react with water to form hydroxide phase which dehydrating forms oxides.

Despite electrophilic carbon sites, molecules of water do not adsorb on tartaric acid and phosphate ions because of their special geometry; (Fig. 4a and c). So hydration is supported by metallic ions that form hydroxides which dehydrate to form oxide phase.

Oxalic solution got the advantage of resisting to corrosion. Except the treatment duration time, the three acids considered pickled almost the same percentage in weight of the coating oxide phase; from 70 to 80%. Nevertheless, for industrial needs, phosphoric solution is the best indicated because of the gain in treatment duration. The resistance to corrosion is also long enough to allow surface dressing to make finished products.

On this purpose, the becoming date of this solution has been studied. Four Hundred cm³ of solution

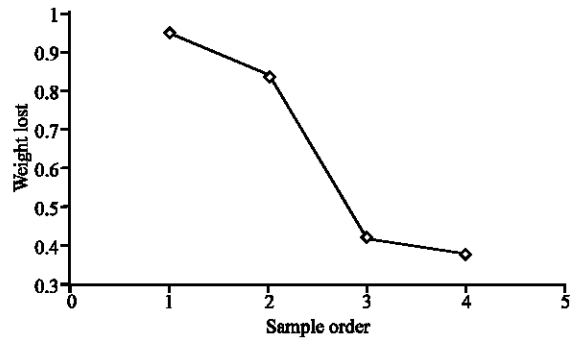


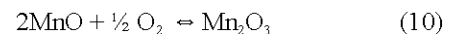
Fig. 5: Phosphoric solution becoming date

have been used to treat samples with 100 g m⁻² corrode rate of known surfaces in the experiment conditions. For each sample the treatment duration was fixed to 10 minutes and the weight lost determined. The solution is considered efficient as long as the weight lost is superior or equal to 0.7%.

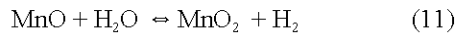
Figure 5 shows that after pickling of samples number 1 and 2 the weight lost becomes weak. The solution is then no longer efficient. The total surface treated with efficiency by 400 cm³ of phosphoric acid 10% volume represents 587.5 cm². That is to say, one litre of this solution can treat with efficiency 15 m² of corroded sheet.

Considering the chemically polished samples, figure 3d shows that for the sample treated in 10 g L⁻¹ solution, the weight after treatment decrease to stabilise for good for any exposure duration. But for solutions more rich of phosphate manganese, samples weight in contrary increase before stabilisation occurs. Explanation of what stands can be given by considering manganese ion that is present. As already indicated, for 10 g L⁻¹ manganese phosphate, the quantity is sufficient to form a complex phase that should protect the metal from oxide formation. During polishing, Mn²⁺ ions react with water to form manganese hydroxide that dehydrates to form MnO, making weight lost appear. When solution presents more manganese, the excess manganese ions remaining on the samples surface and form hydroxide or oxide phase that increase their weight.

In the complex formed, the metallic ions are surrounded by phosphate ions and MnO coming from dehydration of former Mn(OH)₂. So during exposure, MnO that is already present may support any kind of changing coming from the atmosphere. In presence of oxygen, MnO may react to form an oxide of high degree such as:



or with water:



Those reactions taking place increase the complex making it more compact and prevent atmospheric oxygen to reach the metallic phase to form oxide phase.

CONCLUSIONS

Pickling and chemical polishing present some good applicability for corroded carbonaceous steel restoration. During such treatment, formation of a complex at the sample surface occurs. For pickling, tartaric acid solution and phosphoric acid solution permit to restore sample for around 150 and 200 h, respectively before oxidation occur.

With oxalic acid, the complex formed is more protective and samples can stay more than 200 h without oxidation. The oxalate ions uptake the molecules of water, while the negative charges stabilise the metallic ions. In the other solution, complexes formed, phosphate and tartarate ions do not permit adsorption of molecules of water so that, they react with metallic ions to form hydroxide what lead to oxide phases. Any way, all the solution studied for pickling can be used to restore any carbonaceous steel articles before a surface treatment such as enamelling making sure that the treatment should be applied during corrosion resisting duration.

It has also been put to evident that pickling and chemical polishing do not release all the oxide phase from the sample. Formation of a complex with part of this phase occurs maintaining so some metallic ions. This induces enrichment of the metal phase noticed elsewhere (Liu *et al.*, 2003). The passiving character of this complex defines the quality of the treatment for the solution used.

The solution used for chemical polishing reveals to be very performing. The sample treated with stay stable for more than 400 h exposure time. Manganese ion Mn^{2+} is responsible by the way this ion reacts with molecules of water and oxygen preventing then metallic phase to

react. This is in accordance with the reducer character of manganese. The different oxidation states that it presents make it support oxidation while the metallic phase remains protected. This chemical polishing solution has been applied for the utensils restoration with success.

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